Measurement of Surface Tension of Molten Metal under Reducing Gas Atmosphere in Microgravity Condition during Parabolic Flight
— Attempt to Control Oxygen Partial Pressure —

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Abstract

In order to establish technology for precise measurement of surface tension of molten metals under microgravity condition during the parabolic flight of an airplane, copper was selected as the sample from the viewpoints of its oxidization tendency, oxygen partial pressure dependence of surface tension of the molten sample, and ease of heating with electromagnetic levitation. The non-combustibility of the Ar-3vol. %H2 gas that can reduce the oxygen partial pressure of the measurement atmosphere was experimentally confirmed as stipulated in the civil aeronautics law in order to employ it in the parabolic flight experiment. The surface tension of molten copper was successfully measured under the reducing gas atmosphere in microgravity during a parabolic flight experiment for the first time.

Keyword(s): Surface tension, electromagnetic levitation, oxygen partial pressure, parabolic flight, microgravity

1. Introduction

Various high-value-added high-temperature melt processes such as the precision casting of heat resistant turbine blades and the crystal growth of large-diameter semiconductor silicon have become more and more complicated and diversified in recent years to respond to difficult demands for the further improvement of products and manufacturing, e.g. an improvement in the quality and performance of products, cost reductions, energy saving, and a reduction of product manufacturing time. Thus it is indispensable to employ a numerical calculation together with an experiment to optimize the processes. In order to obtain reliable numerical calculation results, accurate thermophysical properties are required. In particular, an accurate surface tension and its temperature coefficient are very important if the process has a free melt surface at which the Marangoni convection appears due to the surface tension gradient.

The oscillating droplet technique using electromagnetic levitation (EML) is one of the most promising methods to measure the accurate surface tension of molten metals1-3). With this technique, metallic sample can be levitated by the Lorentz force generated from the interaction between an electromagnetic field and a loop current at the sample surface induced by the radiofrequency current which flows through the levitation coil. The sample is melted by Joule heating in containerless state.

The major advantages of this technique are to assure measurements free of contaminants from the container, at temperatures sufficiently above the melting point of the sample, and under highly undercooled conditions. This is attributed to the sample not being in contact with the container, which is chemically reactive with the sample at such high temperatures and plays a role in the nucleation center below the melting point. Furthermore, this technique makes it easy to control the oxygen partial pressure (P02) of atmospheric gas, which is an important factor influencing the surface tension of molten metals.

When only the surface tension acts as a restoring force in a levitated droplet without any external force such as gravity, it can be calculated from the frequency of surface oscillation and sample mass using the following the Rayleigh equation4, 5).

\[ \sigma = \frac{3}{8} \pi M v_s^2 \]  

(1)

where \( \sigma \) is the surface tension, \( M \) is the sample mass, and \( v_s \) is the single surface oscillation of \( l = 2 \) mode known as the Rayleigh oscillation.

On the ground, the frequency of the \( l = 2 \) mode splits into three, corresponding to oscillations of \( m = 0, \pm 1, \) and \( \pm 2 \) because of the droplet deformation by gravitational acceleration and electromagnetic forces from the levitation coil. As a result, the effect of the droplet deformation must be calibrated by theoretically derived Cummings and Blackburn equation5.

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within a short time. Furthermore, the melt should not be oxidized even at comparatively high $P_{o_2}$ because only a limited type of gas is acceptable for use in an airplane from the perspective of safety. This is also essential for the viscosity measurement of the droplet under the microgravity condition. In addition to these, it is favorable that the influences of temperature and oxygen partial pressure on surface tension of the candidate sample have been reported even if in only a few reports.

For these reasons, copper was selected as the sample for surface tension measurement under microgravity condition during the parabolic flight experiment. Figure 1 shows the temperature dependence of the equilibrium $P_{o_2}$ of copper oxide, CuO and Cu$_2$O, which were calculated from the following Gibbs energy for formation of these oxides:

$$
\Delta G_{\text{CuO(ox)}} = -306220 + 173.30T \text{ (J mol}$^{-1}$) \text{ (298-1357 K)} \\
\Delta G_{\text{Cu$_2$O(ox)}} = -338300 + 146.63T \text{ (J mol}$^{-1}$) \text{ (298-1357 K)} \\
\Delta G_{\text{CuO$_2$(ox)}} = -380110 + 177.35T \text{ (J mol}$^{-1}$) \text{ (1357-1517 K)} \\
\Delta G_{\text{Cu$_2$O$_2$(ox)}} = -243390 + 87.34T \text{ (J mol}$^{-1}$) \text{ (1517-2000 K)}$$

where $T$ is the temperature. Since a levitated metal droplet usually shows a large undercooling, we assumed that the surface tension of molten copper is measured from an undercooled condition above 1300K, at which the undercooling level is only 58K. In this case, the melt is not oxidized even under comparatively high $P_{o_2}$ of 10$^{-3}$ Pa according to Fig.1.

Figure 2 exhibits the literature data of the influence of $P_{o_2}$ on the surface tension of molten copper at 1373 K and 1383 K. Since a conventional surface tension measurement technique such as the sessile drop method can assure the measurement at a comparatively low temperature to prevent the chemical reaction between the sample and measurement device, high temperature data has not been reported apart from these. In these measurements, the $P_{o_2}$ was mainly controlled by the following gas phase equilibriums for the formation of H$_2$O and CO$_2$:

$$
H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O \\
CO + \frac{1}{2} O_2 \rightleftharpoons CO_2
$$

For comparison, we measured the surface tension of molten copper under Ar-He-3vol.%H$_2$ and Ar-He-10vol.%H$_2$ gases using the EML on the ground in this study. The $P_{o_2}$ of the H$_2$-containing gas varies depending on temperature as in the case of CO-containing gas because the following equilibrium constant for formation of H$_2$O described in the reaction (12), $K_{H_2O}$, has a temperature dependence.

$$
K_{H_2O} = \frac{P_{H_2O}}{P_{H_2}^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}}}
$$

2. Selection of experimental sample and $P_{o_2}$

In order to measure the precise surface tension of molten metals using EML under microgravity during the parabolic flight experiment, it is necessary to clear several limiting conditions. When small Gulfstream-II jet plane operated by Diamond Air Service Inc (Aichi, Japan) is used for the parabolic flight experiment, the roughly 20 seconds of microgravity condition is preceded by a hypergravity condition from 1.5 G to 2.0 G for 20 seconds in order to accelerate the airplane. It is favorable that the sample can be levitated even under this gravity variation to offer greater flexibility to the experiment profile in this case. It is important for the sample to be melted
where $P_{H_2O}$, $P_n$, and $P_{O_2}$ are the partial pressures of gases for H$_2$O, H$_2$, and O$_2$. The temperature dependences of $P_{O_2}$ for these gases were evaluated using the following standard Gibbs energy of formation of H$_2$O$^{16}$, in which the $K_{H_2O}$ was calculated from the $P_{O_2}$ measured by zirconia oxygen sensor operated at 1008K.

$$\Delta G_{H_2O} = -246535 + 54.94T \text{ (J mol}^{-1})$$  \(15\)

The $P_{O_2}$ measured by the oxygen sensor indicated about $10^{-23}$ Pa and $10^{-24}$ Pa for gases of Ar-He-3vol. %H$_2$ and Ar-He-10vol.%H$_2$, respectively. The ratio between the $P_{H_2O}$ and $P_{H_2}$ was assumed to be constant regardless of temperature in evaluation $P_{O_2}$. This figure confirms that the surface tension of molten copper is decreased with increasing $P_{O_2}$. Our measurement results well agree with the literature data. From the results of Fig. 1 and 2, it is essential to clarify the $P_{O_2}$ during the measurement of the surface tension of molten copper. Moreover, it should be less than $10^{-1}$ Pa. However, even if high purity copper is employed in the measurement, it is very difficult to completely eliminate impurities such as aluminum and silicon from the sample. Thus, it is reasonable to suppose that the $P_{O_2}$ should be decreased as low as possible to suppress the formation of oxides of those impurities.

Although there are small differences in the measurement temperature and absolute value of surface tension in Fig. 2, the surface tension seems to become constant when the $P_{O_2}$ is less than $10^{-10}$ Pa. This implies that oxygen adsorption becomes less effective at a $P_{O_2}$ less than $10^{-10}$ Pa. The aim was to control $P_{O_2}$ at less than $10^{-10}$ Pa as a tentative target in this study in order to eliminate the effect of oxygen adsorption. It should be noted here that this $P_{O_2}$ condition of less than $10^{-10}$ Pa can also be applied at temperatures higher than 1373K and 1381K corresponding to Fig. 2 because the oxygen adsorption reaction is exothermic. That is, the influence of $P_{O_2}$ on surface tension becomes small at a higher temperature.

3. Experimental confirmation of non-combustibility of atmospheric gas stipulated in the Japanese Civil Aeronautics Act

As mentioned above, we aimed to control the $P_{O_2}$ at less than $10^{-10}$ Pa for the surface tension measurement of molten copper. In order to decrease the $P_{O_2}$ of atmospheric gas, the gas phase equilibrium such as H$_2$-H$_2$O and CO-CO$_2$ mixtures (see reactions 12 and 13) is usually used$^{11-15,17}$ because it is very difficult to obtain such a very low $P_{O_2}$ even in high-purity commercial inert gas. However, an airplane is not permitted to carry carbon monoxide gas due to its strong toxicity according to the Japanese Civil Aeronautics Act (CAA) (Article 86, Prohibition on Carriage of Explosives etc.). The employment of high concentration hydrogen gas is also prohibited in an airplane by the CAA because of its high combustibility. (When a lower explosive limit of gases mixed with air is less than or equal to 13% at 293K under 101.3kPa of absolute gas pressure, it is defined as an inflammable gas in the CAA.) However if a concentration of hydrogen becomes small by mixing with an inert gas such as argon, it would not be defined as an inflammable gas.

The criterion for dangerous goods that are prohibited to carry into an airplane is specified by the Ministry of Land, Infrastructure, Transport and Tourism in a directive from the CAA. According to this directive, whether gases are "combustible" or "non-combustible" can be determined through the experiment or calculation adopted in ISO 10156/1990 that is prescribed by the International Civil Aviation Organization (ICAO). Besides this method, another experiment method is described concretely in the directive.
In order to employ the Ar-3vol.%H₂ gas defined as nonflammable industrial gas in ISO 10156/1990 in the parabolic flight experiment, the non-combustibility of the gas was experimentally confirmed according to the directive. The results are described in this section. The temperature dependence of \( P_{\text{O}_2} \) of this gas was calculated as shown in Fig. 3 from the method mentioned in the previous section. This confirms that \( P_{\text{O}_2} \) of the gas becomes less than \( 10^{-10} \text{ Pa} \) below 1550K.

Figure 4 shows a schematic diagram of the experimental setup of the combustion test for high pressure gases stipulated in the CAA directive. The experimental apparatus consists of the mixed gas combustor (Fig. 5), gas supply unit, and ignitor. The mixed gas combustor is a double cylinder, in which the sample gas and the air are made to flow through the inner cylinder and outer cylinder, respectively. The inner cylinder has to have an exhaust nozzle of which the internal diameter of its top is 10 mm. The internal diameter of outer cylinder is specified to be 60 mm. Furthermore, a flow straightener for the gases must be mounted inside the cylinders.

The experimental method stipulated in the CAA directive is as follows:

1. The pipe for supplying the sample gas into the mixed gas combustor is evacuated and then backfilled by inert argon gas.

2. The sample gas flows into the combustor together with the air, in which the flow rate of the gases is precisely controlled at 1 cm/s at the outlet of the exhaust nozzle.

3. If spontaneous combustion of the gas is induced by the exposure of the gas to the air, the subsequent procedures should not be carried out.

4. After the streams of the gas and air become stabilized, an electric spark of discharge energy 20 mJ is generated between the needle electrodes positioned at 20 mm from the top center of the nozzle. The existence and non-existence of the gas ignition is the visually judged, with gas ignition defined in this case as the situation whereby the flame is stabilized on the nozzle.

5. When gas ignition is not observed in three repetitions of the same procedure, the above procedures are performed at a sample gas flow rate of 3 cm/s and 5 cm/s while maintaining the flow rate of the air at 1 cm/s.

6. Moreover, if no gas ignition is confirmed even in procedure (5), procedures (1) to (5) are carried out again after the distance of the needle electrodes from the nozzle is reduced to 10 mm.

7. If the ignition of the gas is induced even once by the above procedures, the gas is defined as combustible.

From this experiment, it was confirmed that the Ar-3vol.%H₂ gas is a noncombustible gas, because ignition was never observed in the above experiments. Therefore, the gas is not dangerous goods as specified by the CAA.

4. Surface tension measurement of molten copper under a reducing gas atmosphere in the parabolic flight experiment

As mentioned above, it was confirmed that the Ar-3%H₂ gas is not dangerous goods by the experiment stipulated by the CAA.
The surface tension of molten copper was measured by EML under the Ar-3vol.%H$_2$ gas in the microgravity condition during parabolic flight experiment$^9$. The results are shown in Fig. 6 (■) together with those measured in the terrestrial experiment (▲). The literature data$^{18-20}$ is also shown. The uncertainties for our measurement plot were calculated based on the GUM (ISO Guide to the Expression of Uncertainty in Measurement)$^{21}$, in which the coverage factor of $k_p=2$ was selected. The details of the experimental procedure and facilities can be found in the authors' earlier work$^9$.

The surface tension of molten copper was measured in the temperature range of 1470 K and 1820 K in the terrestrial experiment (▲), which showed a comparatively good linear relationship against temperature. This agrees with the literature results. However it must be noted that there is still room for argument about whether the measurement results show the pure state of surface tension or not. Although it is implied that the $P_{O_2}$ becomes less effective on the surface tension of molten copper at 1371 and 1381K when it is less than 10$^{-10}$ Pa at 1371 K and 1381 K (see Fig. 2), the estimated $P_{O_2}$ of the Ar-3vol.%H$_2$ gas used in this measurement exceeds 10$^{-10}$ Pa above 1550 K as shown in Fig. 3.

We successfully measured the surface tension of molten copper under a reducing atmosphere of H$_2$-containing gas in a microgravity condition prepared by the parabolic flight of an airplane for the first time$^9$. The measurement result comparatively agrees with that of the terrestrial experiment.

However, it shows a small scattering compared with that measured on the ground. Two reasons for this scattering were suggested in our previous work$^9$. The first one is an incorrect estimation of the sample mass required for the surface tension calculation using the Rayleigh equation. Since the solidification of the sample was not finished within the short microgravity period of the parabolic flight experiment, the sample was not collected completely and the droplet fell at 1.5 G after the microgravity condition. Accordingly, the variation of the sample mass during microgravity experiment was estimated from the initial sample mass and the results of the terrestrial experiment. The second possibility is that each calculated surface tension includes the influence of the temperature variation during the measurement. Since the electromagnetic force was significantly decreased under the microgravity condition to eliminate the influence of droplet deformation on surface oscillation, the temperature of droplet inevitably decreased by about 9K during the measurement.

In addition to these reasons, we would like to focus attention on the possibility of influence of $P_{O_2}$ prepared by Ar-3vol.%H$_2$ gas in this manuscript. In our parabolic flight experiment, the $P_{O_2}$ of the Ar-3vol.%H$_2$ gas was passively decided through the gas phase equilibrium described in reaction (12) depending on the amount of H$_2$O contained as impurity because it was not actively mixed into the gas. The volume content of H$_2$O existing as an impurity in the gas was calculated to be about 0.024% from the standard Gibbs energy for formation of H$_2$O (eq. 15) using the $P_{O_2}$ value of 10$^{-19}$ Pa measured by the oxygen sensor operated at 1008K. This calculation method is the same as that for the temperature dependence of $P_{O_2}$ corresponding to Fig 3.

Since the H$_2$O content in the gas was originally very little in this experiment, the ratio between the $P_{H_2O}$ and $P_{H_2}$ is sensitively changed by even an extremely small variation in the quantity of H$_2$O. It becomes difficult to assume that the ratio is constant regardless of temperature in this case. As a result, the $P_{O_2}$ of the gas is also strongly influenced through reaction (12).

For example, H$_2$O is dissociated corresponding to the temperature due to the temperature dependence of equilibrium constant $K_{H_2O}$ (see eq. 14). Furthermore, the distance from the gas supply system mounted on the airplane to our experimental facility is much longer than that for in the terrestrial experiment. In addition the gas supply system mounted on the airplane is used for various occasions between many users. Thus, it is necessary to pay full attention to the influence of physically adsorbed moisture inside the long pipes which carry the atmospheric gas during the measurement of surface tension.

Furthermore Kakikura et al.$^{21}$ suggested that the $P_{O_2}$ at the droplet surface is influenced by gas flow conditions such as inlet velocity and flow direction when the gravity level is significantly changed during the parabolic flight experiment.

In order to eliminate the influence of the variation of $P_{O_2}$ due to an extremely small variation in the quantity of H$_2$O in the parabolic flight experiment, we suggest that moisture should be actively mixed into the Ar-3vol.%H$_2$ gas using a vaporizer in
future studies. For example, if the volume fraction of $\text{H}_2\text{O}$ is increased from 0.024% to 1% in the gas, the $P_{\text{O}_2}$ of the gas is not influenced by a small amount of dissociation of $\text{H}_2\text{O}$ at high temperature because the variation of the ratio between $P_{\text{H}_2\text{O}}$ and $P_{\text{H}_2}$ becomes negligibly small due to the small variation in the quantity of the $\text{H}_2\text{O}$. It is also acceptable for a desorbed $\text{H}_2\text{O}$ from the gas pipes.

Although the $P_{\text{O}_2}$ of the Ar-3vol.%$\text{H}_2$ gas inevitably increased due to the gas phase equilibrium of the reaction (12) as shown in Fig. 7 when the moisture content is increased, the $P_{\text{O}_2}$ value can be selected by controlling the amount of mixed moisture according to the temperature. As a result, the surface tension measurement at an isothermal condition and iso-$P_{\text{O}_2}$ condition can be expected under a microgravity condition as shown by the dashed line and dotted line, respectively.

5. Summary

The surface tension measurements of molten metal using the EML under microgravity condition during the parabolic flight of an airplane were described in this manuscript. Copper was selected as the sample for the parabolic flight experiment from the viewpoint of its oxidization tendency, the influence of oxygen partial pressure, and ease of melting and electromagnetic levitation. Since it was confirmed that the Ar-3vol.%$\text{H}_2$ gas is not dangerous by the experiment stipulated in the Civil Aeronautics Act, it was employed in the parabolic flight experiment to decrease the $P_{\text{O}_2}$. Although the surface tension of molten copper measured under microgravity condition was similar to that measured on the ground, it showed a small scattering due to the incorrect estimation of the sample mass and temperature variation during the measurement. We also pointed out that the $P_{\text{O}_2}$ of the Ar-3vol.%$\text{H}_2$ gas is influenced by even an extremely small variation in the quantity of $\text{H}_2\text{O}$. Furthermore, we suggested that moisture should be actively mixed into the Ar-3vol.%$\text{H}_2$ gas to decrease a large sensitivity of the $P_{\text{O}_2}$ of the gas to an extremely small variation in the quantity of $\text{H}_2\text{O}$.

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